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(54) Title: CURABLE SILICONE COMPOSITION AND CURED PRODUCT THEREFROM

(57) **Abstract:** A curable silicone composition comprising: (A) an organopolysiloxane that is represented by the average unit formula:  $(R_1^3SiO_{1/2})_a(R_2^2SiO_{2/2})_b(R_3^3SiO_{3/2})_c(SiO_{4/2})_d$  (wherein  $R_1^3$ ,  $R_2^2$ , and  $R_3^3$  are each independently selected from substituted or unsubstituted monovalent hydrocarbon groups and epoxy-functional monovalent organic groups, with the proviso that at least 20 mole% of  $R_1^3$  are aryl groups, and a, b, c, and d are numbers that satisfy  $0 \leq a \leq 0.8$ ,  $0 \leq b \leq 0.8$ ,  $0.2 \leq c \leq 0.9$ ,  $0 \leq d < 0.8$ , and  $a + b + c + d = 1$ ), and that has at least two of the aforementioned epoxy-functional monovalent organic groups in each molecule; (B) a compound that has a group capable of reacting with the epoxy group; (C) a cure accelerator; and (D) a thermally conductive filler, has excellent handling characteristics and that cures rapidly to give a cured product that is highly thermally conductive, very flexible, highly adhesive, and very flame retardant.

DESCRIPTION

## CURABLE SILICONE COMPOSITION AND CURED PRODUCT THEREFROM

Technical Field

[0001] The present invention relates to a curable silicone composition and to a cured product therefrom. The present invention more particularly relates to a curable silicone composition that has excellent handling characteristics and that cures rapidly to give a cured product that is highly thermally conductive, very flexible, highly adhesive, and very flame retardant. The present invention also more particularly relates to a cured product that is highly thermally conductive, very flexible, and very flame retardant.

10 [0002] There have been investigations into the incorporation of thermally conductive filler into the curable epoxy resin compositions used as sealants and adhesives for electrical/electronic components and into the utilization of the resulting compositions as adhesives for bonding a heat source, such as a semiconductor chip, to a heat sink member. 15 The cured products from such compositions, however, have had a high modulus and have been stiff, which has quite readily resulted in the generation of large stresses on the electrical/electronic component, such as a semiconductor chip, due to thermal expansion of the cured material. This has resulted in problems such as warping of the electrical/electronic component or substrate, the appearance of cracks in the cured product 20 itself, the generation of gaps between the electrical/electronic component and the cured product, and even in failure of the electrical/electronic component. Moreover, while this cured product needs to be flame retardant, the flame retardancy has been inadequate.

[0003] In order to reduce the stress associated with the cured product, die-attach pastes comprising epoxy resin and the reaction product of cyanate resin with an epoxy-functional 25 dimethylsiloxane compound (refer to Japanese Laid-Open (Unexamined) Patent Application Numbers Hei 10-147764 (147,764/1998) and Hei 10-163232 (163,232/1998)) and die-bonding agents comprising the reaction product of epoxy-functional silicone oil and a phenolic organic compound (refer to Japanese Laid-Open (Unexamined) Patent Application Numbers Hei 7-22441 (22,441/1995), Hei 7-118365 (118,365/1995), and Hei 30 10-130465 (130,465/1998)) have been introduced. However, the cured products afforded by these materials are still stiff and the stress-reducing effect is inadequate.

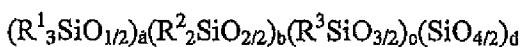
**[0004]** In another vein, curable silicone compositions provide cured products that have excellent electrical characteristics, e.g., dielectric characteristics, volumetric resistivity, and dielectric breakdown strength, and for this reason are used as sealants and adhesives for electrical/electronic components. However, they yield cured products that are, 5 conversely, soft and that have a low mechanical strength and a low modulus, and this has resulted in a poor capacity to protect electrical/electronic components, that is, a poor performance with regard to protecting electrical/electronic components from external impact or shock. In addition, these cured products, because they exhibit low adhesiveness for electrical/electronic components, have been associated with the facile generation of 10 gaps between the cured product and these components. While there have been attempts at improving the modulus and mechanical strength of the cured product by incorporating filler into the curable silicone composition, this results in a loss of the softness and flexibility. The generation of thermal conductivity through the incorporation of metal powder (e.g., silver, copper, and so forth) into curable silicone compositions has been 15 studied, but this approach results in a low flame retardancy by the cured material thereby afforded.

**[0005]** Japanese Laid-Open (Unexamined) Patent Application Number Hei 6-306084 (306,084/1994) discloses a curable silicone composition that has a short gelation time; this 20 curable silicone composition comprises epoxy-modified silicone oil and phenol-modified silicone oil. This curable silicone composition, however, exhibits a poor curability and requires a lengthy period of heating for cure. In addition, it generates a very brittle cured product.

**[0006]** It is an object of the present invention to provide a curable silicone composition that has excellent handling characteristics and that cures rapidly to give a cured product 25 that is highly thermally conductive, very flexible, highly adhesive, and very flame retardant. It is a further object of the present invention is to provide a cured product that is highly thermally conductive, very flexible, and very flame retardant.

#### Disclosure of Invention

**[0007]** The curable silicone composition of the present invention comprises: 30 (A) an organopolysiloxane that is represented by the average unit formula:



(wherein R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently selected from substituted or unsubstituted monovalent hydrocarbon groups and epoxy-functional monovalent

organic groups, with the proviso that at least 20 mole% of  $R^3$  are aryl groups, and  $a$ ,  $b$ ,  $c$ , and  $d$  are numbers that satisfy  $0 \leq a \leq 0.8$ ,  $0 \leq b \leq 0.8$ ,  $0.2 \leq c \leq 0.9$ ,  $0 \leq d < 0.8$ , and  $a + b + c + d = 1$ ),  
and that has at least two of the aforementioned epoxy-functional monovalent organic  
5 groups in each molecule;

- (B) a compound that has a group capable of reacting with the epoxy group;
- (C) a cure accelerator; and
- (D) a thermally conductive filler.

[0008] The cured product of the present invention is characteristically afforded by cure  
10 of the composition described above.

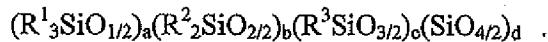
#### Effects of Invention

[0009] The curable silicone composition of the present invention characteristically has excellent handling characteristics and cures rapidly to give a cured product that is highly thermally conductive, very flexible, highly adhesive, and very flame retardant. The cured  
15 product of the present invention is characterized by an excellent thermal conductivity, an excellent flexibility, and an excellent flame retardancy.

#### Detailed Description of the Invention

[0010] The curable silicone composition of the present invention will be described in detail first.

20 [0011] Component (A), which is a main component of the composition, is organopolysiloxane represented by the average unit formula:



$R^1$ ,  $R^2$ , and  $R^3$  in this formula are each independently selected from substituted or unsubstituted monovalent hydrocarbon groups and epoxy-functional monovalent organic  
25 groups. The subject monovalent hydrocarbon groups can be exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, and so forth; alkenyl groups such as vinyl, allyl, butenyl, pentenyl, hexenyl, and so forth; aryl groups such as phenyl, tolyl, xylyl, and so forth; aralkyl groups such as benzyl, phenethyl, and so forth; and halogenated alkyl groups such as chloromethyl, 3,3,3-trifluoropropyl, and so forth. Alkyl groups and aryl  
30 groups are preferred, and methyl and phenyl are particularly preferred. The epoxy-functional monovalent organic groups can be exemplified by glycidoxylalkyl groups such as 2-glycidoxethyl, 3-glycidoxpropyl, 4-glycidoxbutyl, and so forth;

epoxycycloalkylalkyl groups such as 2-(3,4-epoxycyclohexyl)ethyl, 3-(3,4-epoxycyclohexyl)propyl, 2-(3,4-epoxy-3-methylecyclohexyl)-2-methylethyl, and so forth; and oxiranylalkyl groups such as 4-oxiranylbutyl, 8-oxiranyloctyl, and so forth.

Glycidoxyalkyl groups and epoxycycloalkylalkyl groups are preferred, and 3-glycidoxypropyl and 2-(3,4-epoxycyclohexyl)ethyl are particularly preferred.

[0012] At least 20 mol% of the  $R^3$  in the preceding formula must be aryl groups, and preferably at least 50 mol% and particularly preferably at least 80 mol% are aryl groups. Problems such as a decline in the compatibility with component (B), a decline in the adhesiveness of the resulting composition, and a decline in the mechanical strength of the ultimately obtained cured product occur when the proportion of aryl groups in  $R^3$  is below the lower limit of the given range. Phenyl is particularly preferred for the aryl groups encompassed by  $R^3$ .

[0013]  $a$ ,  $b$ ,  $c$ , and  $d$  in the preceding formula are numbers that satisfy the following:  $0 \leq a \leq 0.8$ ,  $0 \leq b \leq 0.8$ ,  $0.2 \leq c \leq 0.9$ ,  $0 \leq d < 0.8$ , and  $a + b + c + d = 1$ .  $a$  is a number that represents the proportion of the  $R^1_3SiO_{1/2}$  siloxane unit in component (A). When component (A) is composed of only the  $R^3SiO_{3/2}$  siloxane unit, its viscosity becomes elevated and the handling characteristics of the resulting composition deteriorate, and for this reason  $a$  is a number preferably satisfying  $0 < a \leq 0.8$  and more preferably  $0.3 \leq a \leq 0.8$ .  $b$  is a number that represents the proportion of the  $R^2_2SiO_{2/2}$  siloxane unit in component (A) and preferably is a number satisfying  $0 \leq b \leq 0.6$  because this impedes outmigration of component (A) from the resulting cured product at suitable molecular weights and also yields cured product with an excellent mechanical strength.  $c$  is a number that represents the proportion of the  $R^3SiO_{3/2}$  siloxane unit in component (A) and is preferably a number satisfying  $0.4 \leq c \leq 0.9$  because this provides the instant composition with good handling characteristics and a good adhesiveness and provides the cured product therefrom with a good mechanical strength and a good flexibility.  $d$  is a number that represents the proportion of the  $SiO_{4/2}$  siloxane unit in component (A) and is preferably  $0 \leq d < 0.2$  because this provides the composition with good handling characteristics and a good adhesiveness and provides the cured product therefrom with a good mechanical strength and a good flexibility.

[0014] Component (A) must have at least two of the aforementioned epoxy-functional monovalent organic groups in each molecule. While the content of epoxy-functional monovalent organic group in component (A) is not otherwise specifically limited, the

epoxy equivalent weight of component (A) (the value afforded by dividing the mass-average molecular weight of component (A) by the number of epoxy groups in the molecule) is preferably in the range from 100 to 2,000, is more preferably in the range from 100 to 1,000, and particularly preferably is in the range from 100 to 700. The 5 flexibility of the cured product declines when the epoxy equivalent weight is below the lower limit on the aforementioned range, while exceeding the upper limit on this range results in a decline in the adhesiveness and curability of the resulting composition and in a decline in the mechanical strength of the cured product. Component (A) may be a single organopolysiloxane or a mixture of two or more organopolysiloxanes. The state of 10 component (A) at 25°C is not critical, and it can be, for example, a liquid or solid. Solid component (A) can be mixed to homogeneity with the other components through the use of an organic solvent or by heating. Component (A) is preferably a liquid at 25°C because this provides a good blendability with the other components and provides good handling characteristics. The mass-average molecular weight of component (A) is not critical, but is 15 preferably in the range of 500 to 10,000 and particularly preferably is in the range of 750 to 3,000.

**[0015]** The following organopolysiloxanes are examples of component (A). **a**, **b**, **c**, and **d** in these formulas are defined as above, except that **a** and **b** in the following formulas are not zero. **e** and **f** in these formulas are numbers that satisfy the following conditions:

20  $0.1 < e < 0.8$ ,  $0 < f < 0.2$ ,  $0.2 \leq e + f \leq 0.9$ , and  $0.2 \leq e/(e + f)$ . X in the following formulas represents 3-glycidoxypipropyl and Y represents 2-(3,4-epoxycyclohexyl)ethyl.

**[0016]**

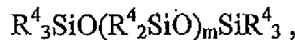
[X(CH<sub>3</sub>)<sub>2</sub>SiO<sub>1/2</sub>]<sub>a</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>c</sub>  
 [Y(CH<sub>3</sub>)<sub>2</sub>SiO<sub>1/2</sub>]<sub>a</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>c</sub>  
 25 [X(CH<sub>3</sub>)<sub>2</sub>SiO<sub>1/2</sub>]<sub>a</sub>[(CH<sub>3</sub>)<sub>2</sub>SiO<sub>2/2</sub>]<sub>b</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>c</sub>  
 [Y(CH<sub>3</sub>)<sub>2</sub>SiO<sub>1/2</sub>]<sub>a</sub>[(CH<sub>3</sub>)<sub>2</sub>SiO<sub>2/2</sub>]<sub>b</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>c</sub>  
 [XCH<sub>3</sub>SiO<sub>2/2</sub>]<sub>b</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>c</sub>  
 [YCH<sub>3</sub>SiO<sub>2/2</sub>]<sub>b</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>c</sub>  
 [X(CH<sub>3</sub>)<sub>2</sub>SiO<sub>1/2</sub>]<sub>a</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>e</sub>[CH<sub>3</sub>SiO<sub>3/2</sub>]<sub>f</sub>  
 30 [Y(CH<sub>3</sub>)<sub>2</sub>SiO<sub>1/2</sub>]<sub>a</sub>[C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>e</sub>[CH<sub>3</sub>SiO<sub>3/2</sub>]<sub>f</sub>  
 [C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>e</sub>[XSiO<sub>3/2</sub>]<sub>f</sub>  
 [C<sub>6</sub>H<sub>5</sub>SiO<sub>3/2</sub>]<sub>e</sub>[YSiO<sub>3/2</sub>]<sub>f</sub>

[0017] The method for preparing component (A) is not critical and can be exemplified by the following methods: the co-hydrolysis and condensation reaction of phenyltrialkoxysilane and alkoxy silane having an epoxy-functional monovalent organic group, e.g., 3-glycidoxypropyltrimethoxysilane or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane; the alcohol-eliminating condensation reaction of the aforementioned alkoxy silane having an epoxy-functional monovalent organic group with a silanol-functional organopolysiloxane prepared by the hydrolysis and condensation of phenyltrichlorosilane or phenyltrialkoxysilane; a hydrosilylation reaction between olefin having an epoxy-functional monovalent organic group and SiH-functional organopolysiloxane prepared by co-hydrolysis and condensation of phenyltrichlorosilane or phenyltrialkoxysilane in the presence of an SiH-functional silane such as dimethylchlorosilane; an equilibration reaction in the presence of a base catalyst between (i) organopolysiloxane prepared by the hydrolysis and condensation of phenyltrichlorosilane or phenyltrialkoxysilane and (ii) trimethylsiloxy-endblocked methyl(3-glycidoxypropyl)siloxane-dimethylsiloxane copolymer or trimethylsiloxy-endblocked methyl{2-(3,4-epoxycyclohexyl)ethyl}siloxane-dimethylsiloxane copolymer; an equilibration reaction in the presence of a base catalyst between organopolysiloxane comprising the  $C_6H_5SiO_{3/2}$  siloxane unit and cyclic methyl(3-glycidoxypropyl)siloxane or cyclic methyl{2-(3,4-epoxycyclohexyl)ethyl}siloxane; and an equilibration reaction in the presence of an acid or base catalyst among organopolysiloxane comprising the  $C_6H_5SiO_{3/2}$  siloxane unit and cyclic methyl(3-glycidoxypropyl)siloxane or cyclic methyl{2-(3,4-epoxycyclohexyl)ethyl}siloxane and cyclic dimethylsiloxane.

[0018] Component (B), which is a compound that contains a group capable of reacting with the epoxy group, reacts with the epoxy groups in component (A) to bring about curing of the composition. This group capable of reacting with the epoxy group can be exemplified by the primary amino group, secondary amino group, hydroxyl group, phenolic hydroxyl group, carboxylic acid group, acid anhydride group, mercapto group, and silanol group. The phenolic hydroxyl group is preferred from the standpoint of reactivity and pot life. Component (B) can be specifically exemplified by phenol compounds such as phenol-novolac resins, cresol-novolac resins, bisphenol A compounds, and so forth, and by phenolic hydroxyl-functional organosiloxanes. Phenolic hydroxyl-functional organosiloxanes are preferred, and organosiloxane containing at least two phenolic hydroxyl groups in each molecule is particularly preferred. The phenol equivalent

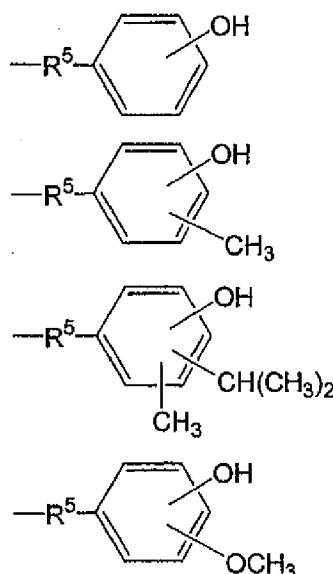
weight of component (B) (the value afforded by dividing the mass-average molecular weight of component (B) by the number of phenolic hydroxyls in a single molecule) is preferably not more than 1,000 and particularly preferably is not more than 500 for the high reactivity.

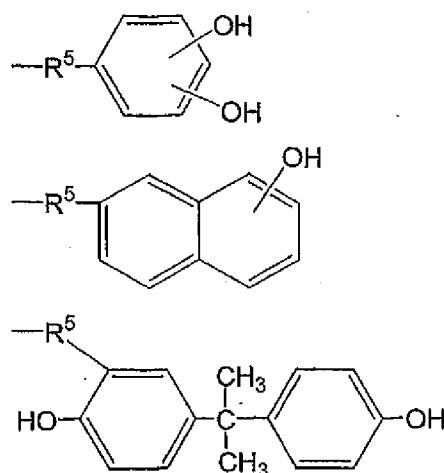
5 [0019] The phenolic hydroxyl-functional organosiloxane encompassed by component (B) is preferably organosiloxane with the general formula:



because this can improve the flexibility of the cured product from the composition. Each R<sup>4</sup> in this formula is independently selected from substituted or unsubstituted monovalent hydrocarbon groups and phenolic hydroxyl-functional monovalent organic groups. This monovalent hydrocarbon groups can be exemplified by the same groups as provided above, and preferably is alkyl groups or aryl groups and particularly preferably is methyl or phenyl. The phenolic hydroxyl-functional organic groups can be exemplified by the groups presented below. At least two of the R<sup>4</sup> in each molecule are phenolic hydroxyl-functional organic groups. R<sup>5</sup> in the structures is a divalent organic group and can be specifically exemplified by alkylene groups such as ethylene, methylethylene, propylene, butylene, pentylene, and hexylene; and by alkyleneoxyalkylene groups such as ethylenoxyethylene, ethylenoxypropylene, ethylenoxybutylene, and propylenoxypropylene, wherein alkylene groups are preferred and propylene is particularly preferred.

20 [0020]

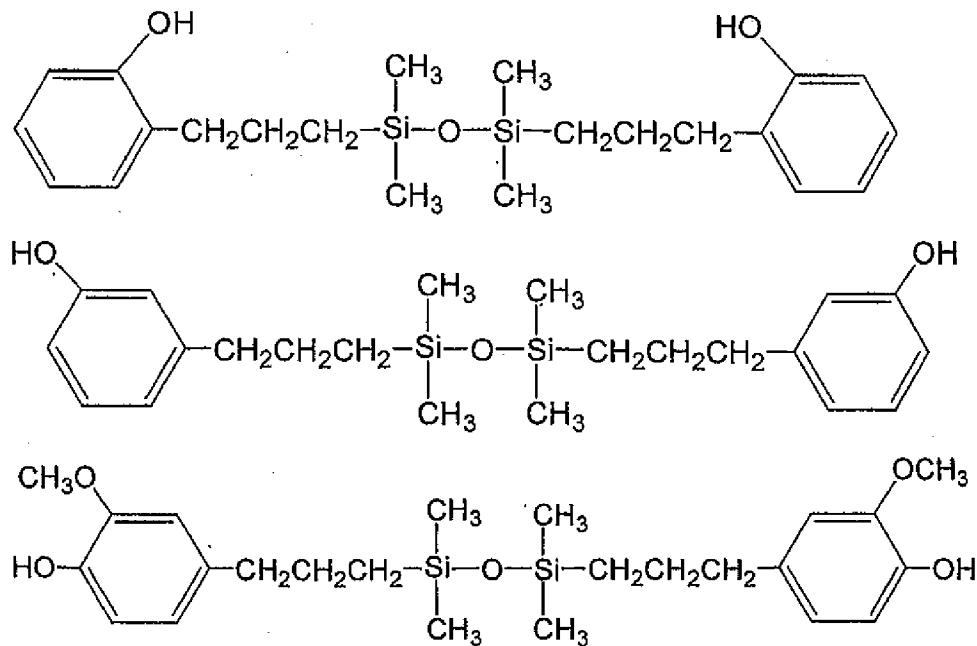




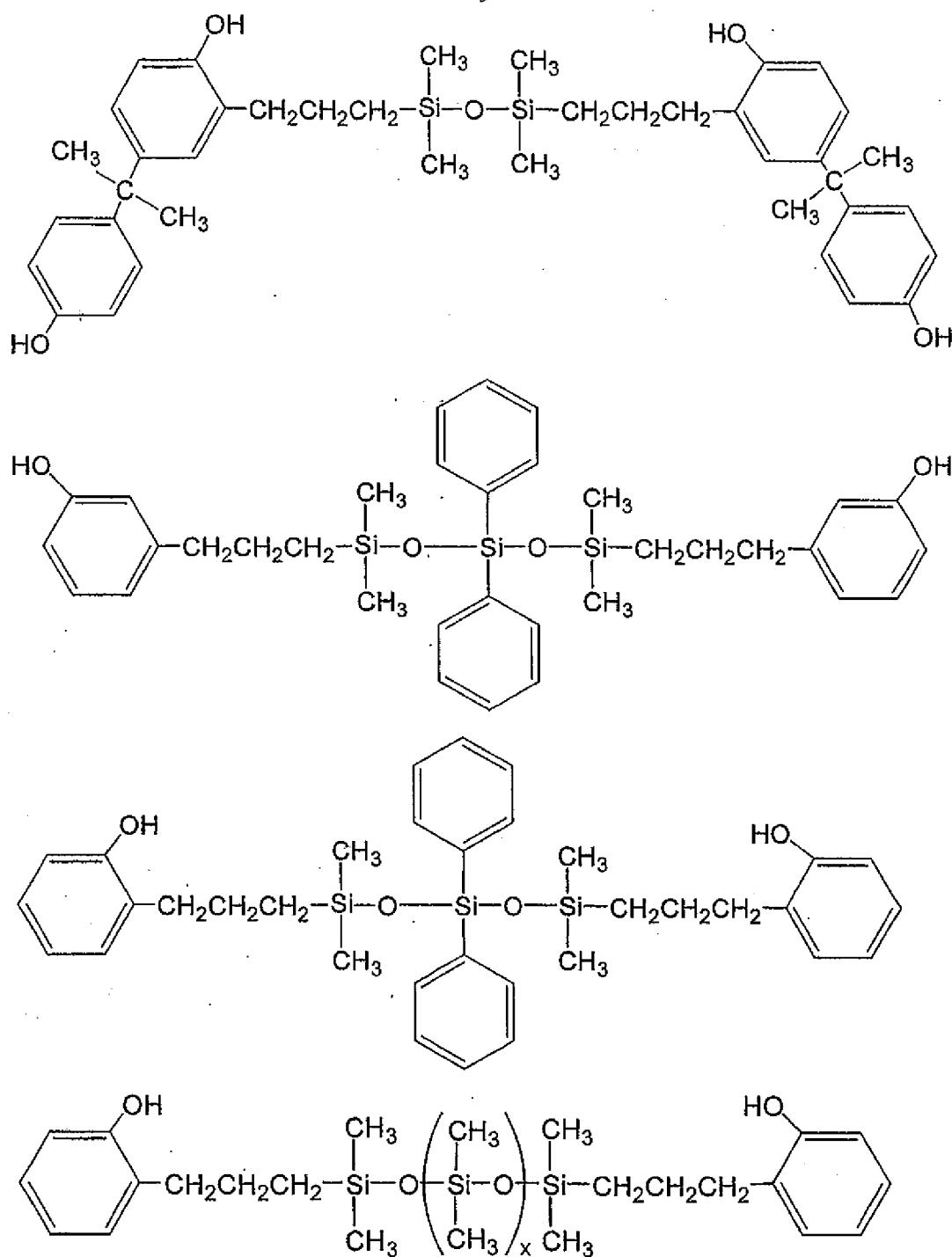
[0021] **m** in the preceding formula is an integer from 0 to 1,000 and preferably is an integer from 0 to 100 and particularly preferably is an integer from 0 to 20. When **m** exceeds the upper limit on this range, the handling characteristics decline, the blendability into component (A) declines, and dilution of the resulting composition with, for example, organic solvent, may also be necessary.

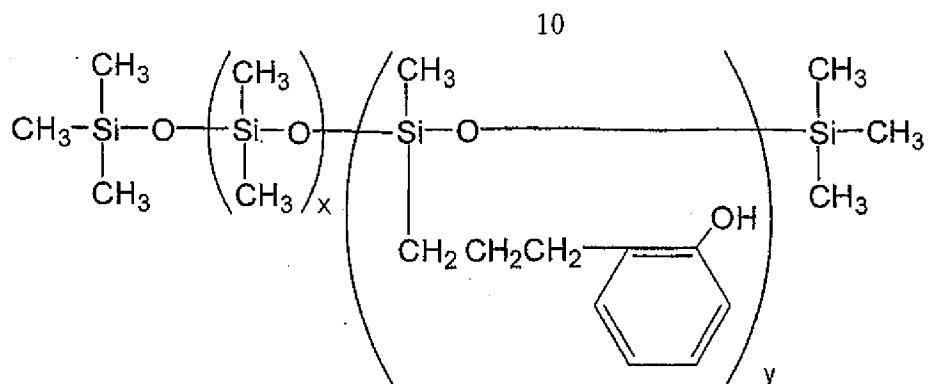
[0022] The organosiloxane encompassed by component (B) can be exemplified by the organosiloxanes provided below. **x** in the formulas is an integer from 1 to 20 and **y** is an integer from 2 to 10.

[0023]



9





**[0024]** The method for preparing component (B) is not critical and can be exemplified by a hydrosilylation reaction between an alkenyl-functional phenol compound and SiH-functional organopolysiloxane.

5   **[0025]** The state of component (B) at 25°C is not critical and component (B) can be a liquid or solid; however, it is preferably a liquid for the ease of handling this provides. When component (B) is a liquid at 25°C, its viscosity is preferably in the range of 1 to 1,000,000 mPa·s and particularly preferably is in the range of 10 to 5,000 mPa·s. The mechanical strength of the cured product declines when the viscosity at 25°C falls below 10 the lower limit on the aforementioned range, while the handling characteristics of the resulting composition decline when the upper limit on the aforementioned range is exceeded.

15   **[0026]** The content of component (B) is not specifically limited, but is preferably 0.1 to 500 parts by mass and particularly preferably is 0.1 to 200 parts by mass, in each case per 100 parts by mass of component (A). When component (B) contains phenolic hydroxyl, component (B) is then used in an amount that provides a molar ratio of phenolic hydroxyl in component (B) to total epoxy in the composition of preferably 0.2 to 5, more preferably 0.3 to 2.5, and particularly preferably 0.8 to 1.5. It becomes increasingly difficult to obtain a thorough cure for the resulting composition when the molar ratio of 20 phenolic hydroxyl in component (B) to total epoxy in the composition falls below the lower limit on the given range, while the mechanical properties of the cured product decline substantially at above the upper limit on the given range.

25   **[0027]** Component (C) is a cure accelerator that accelerates the reaction between the epoxy groups in component (A) and the group in component (B) capable of reacting with the epoxy group, i.e., the curing reaction of the composition. Component (C) can be exemplified by tertiary amine compounds; organometal compounds, e.g., of aluminum or zirconium; organophosphorus compounds such as phosphine; and also by heterocyclic

amine compounds, boron complex compounds, organoammonium salts, organosulfonium salts, organoperoxides, and reaction products from the preceding. Examples here are phosphorus compounds such as triphenylphosphine, tributylphosphine, tri(p-methylphenyl)phosphine, tri(nonylphenyl)phosphine, triphenylphosphine/triphenylborate, 5 tetraphenylphosphine/tetraphenylborate, and so forth; tertiary amine compounds such as triethylamine, benzylidemethylamine,  $\alpha$ -methylbenzylidemethylamine, 1,8-diazabicyclo[5.4.0]undecene-7, and so forth; and imidazole compounds such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, and so forth. The use of an encapsulated cure accelerator is preferred because this enables a lengthening of the 10 composition's use time. A commercially available encapsulated cure accelerator is encapsulated amine-type cure accelerator comprising an amine-type cure accelerator incorporated in bisphenol A-type epoxy resin (for example, HX-3088 from Asahi Kasei Corporation).

**[0028]** The content of component (C) is not specifically limited, but preferably is no 15 more than 50 parts by mass, more preferably is 0.01 to 50 parts by mass, and particularly preferably is 0.1 to 5 parts by mass, in each case per 100 parts by mass of component (A). It becomes increasingly difficult to obtain a thorough cure for the resulting composition when the content of component (C) falls below the lower limit on the given range, while the mechanical properties of the cured product decline substantially at above the upper 20 limit on the given range.

**[0029]** Component (D) is a thermally conductive filler that imparts thermal 25 conductivity and flame retardancy to the cured product from the composition. Component (D) can be exemplified by the very finely divided powders of metals such as gold, silver, nickel, copper, and so forth; very finely divided powders afforded by the vapor deposition or plating of a metal, e.g., gold, silver, nickel, copper, and so forth, on the surface of a very finely divided powder of, e.g., ceramic, glass, quartz, organic resin, and so forth; metal compounds such as aluminum oxide, aluminum nitride, zinc oxide, and so forth; and mixtures of two or more of the preceding. Metal powders are preferred for the high thermal conductivity they provide. The metal powders can be exemplified by the powders of gold, 30 silver, copper, aluminum, nickel, palladium, and their alloys, and also by the powders of brass, shape-memory alloys, solder, and mixtures of two or more of the preceding. Silver powder is particularly preferred for the good thermal conductivity, electrical conductivity, and blendability it provides. Its shape is not critical and can be exemplified by ground

shapes, spheres, fibrous shapes, columns, flakes, scales, plates, and coils. The particle size is also not critical, but the maximum particle size is generally no more than 200  $\mu\text{m}$  and the average particle size is preferably in the range from 0.001 to 50  $\mu\text{m}$ . Combinations of two or more types of silver powder can also be used.

5 [0030] The content of component (D) is not critical; however, in order to avoid a loss of fluidity by the composition, the content of component (D) is preferably in the range of 100 to 5,000 parts by mass, more preferably in the range of 500 to 5,000 parts by mass, and particularly preferably in the range of 500 to 4,000 parts by mass, in each case per 100 parts by mass of the total of components (A) and (B).

10 [0031] The composition may contain a filler (E) other than component (D) in order to improve the mechanical strength of the cured product afforded by the composition. Component (E) can be exemplified by fibrous fillers such as glass fibers, alumina fibers, alumina/silica ceramic fibers, boron fibers, zirconia fibers, silicon carbide fibers, metal fibers, and so forth; particulate fillers such as fused silica, crystalline silica, precipitated

15 silica, fumed silica, calcined silica, zinc oxide, calcined clay, carbon black, glass beads, alumina, talc, calcium carbonate, clay, aluminum hydroxide, magnesium hydroxide, barium sulfate, aluminum nitride, boron nitride, silicon carbide, aluminum oxide, magnesium oxide, titanium oxide, beryllium oxide, kaolin, mica, zirconia, and so forth; and mixtures of two or more of the preceding. The average particle size and shape of

20 component (E) are not critical, but spherical silica with an average particle size of 0.1 to 40  $\mu\text{m}$  is preferred for the excellent moldability this provides. The content of component (E) is also not critical, but is preferably no greater than 10 parts by mass and particularly preferably is 0.01 to 10 parts by mass, in each case per 100 parts by mass of component (A).

25 [0032] A coupling agent, for example, a silane coupling agent or titanate coupling agent, can also be incorporated in order to bring about good dispersion by component (D) in component (A) or (B) or their mixture and in order to improve the adhesiveness for substrate when the composition undergoes cure. The silane coupling agents can be exemplified by epoxy-functional alkoxy silanes such as 3-

30 glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and so forth; amino-functional alkoxy silanes such as N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-phenyl-3-aminopropyltrimethoxysilane, and so forth; and mercapto-functional

alkoxysilanes such as 3-mercaptopropyltrimethoxysilane, and so forth. The titanate coupling agents can be exemplified by isopropoxytitanium tri(isostearate), and so forth. The content of coupling agent is not critical, but is preferably no more than 10 parts by mass and particularly preferably is 0.01 to 10 parts by mass, in each case per 100 parts by mass of component (A).

5 [0033] Other optional components that may be incorporated include alkoxy silanes such as tetramethoxysilane, tetraethoxysilane, dimethyldimethoxysilane, methylphenyldimethoxysilane, methylphenyldiethoxysilane, phenyltrimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, and so forth; and organic solvents such as aliphatic solvents, e.g., hexane, heptane, and so forth; aromatic solvents, e.g., toluene, xylene, and so forth, and ketone solvents, e.g., methyl ethyl ketone, methyl isobutyl ketone, and so forth.

10 [0034] The composition can be prepared by mixing components (A), (B), (C), and (D) and as necessary any optional components to homogeneity. The mixing procedure is not critical and can be exemplified by simultaneously mixing components (A), (B), (C), and (D) and as necessary any optional components; premixing components (A) and (B) and then blending in components (C) and (D) and as necessary any optional components; and premixing components (A), (B), and (D) and as necessary any optional components and then blending in component (C). The device for mixing components (A), (B), (C), and (D) and as necessary any optional components is not critical and can be exemplified by single- and twin-shaft continuous mixers, two-roll mills, Ross mixers®, Hobart mixers, dental mixers, planetary mixers, and kneader mixers.

15 [0035] The composition, because it exhibits good handling characteristics and cures rapidly, can be used by such methods as transfer molding, injection molding, potting, casting, powder coating, immersion coating, dripping, and so forth. Liquids and pastes are preferred because this enables selection from a variety of use methods, such as potting, screen printing, coating, and so forth; and also supports facile adaptation to low-volume applications.

20 [0036] The cured product of the present invention will now be described in detail.

25 [0037] The cured product of the present invention is characteristically afforded by the cure of a curable silicone composition as described in the preceding.

[0038] This cured product is useful as a heat-radiating material between a semiconductor device and a heat sink and as a sealant resin for electrical/electronic components. In particular, this cured product, by virtue of its excellent thermal conductivity, flexibility, and flame retardancy, is very useful as an adhesive between a 5 semiconductor device and a heat sink.

Examples

[0039] The curable silicone composition and cured product therefrom of the present invention will now be described using Practical Examples and Comparative Examples. The properties of the curable silicone compositions and cured products were measured by the 10 following methods.

Viscosity

[0040] The viscosity at 25°C was measured at 2.5 rpm using an E-type viscometer (Digital Viscometer DV-U-E, Model II, from Tokimec Inc.).

Mass-average molecular weight

[0041] The mass-average molecular weight was measured on a toluene solution of the 15 organopolysiloxane using gel permeation chromatographic analysis calibrated with polystyrene standards.

Complex viscoelastic modulus

[0042] The curable silicone composition was filled into a mold that had a cavity with 20 dimensions of width 10 mm × length 50 mm × depth 2 mm. After degassing at 70 mmHg, press curing was carried out for 60 minutes at 150°C under the pressure of 2.5 MPa. Secondary heating in an oven for 2 hours at 180°C then gave the cured product test specimen. The complex viscoelastic modulus at 25°C was measured on this test specimen 25 using an ARES Rheometer (product of Rheometric Scientific Inc.) at a 0.5% torsion, oscillation of 1 Hz, and a temperature rise from -50°C to 150°C at a rate of temperature rise of 3°C/minute.

Adhesiveness

[0043] A solder resist (developable solder resist, PSR-4000 CC02/CA-40 CC02, from 30 Taiyo Ink Mfg. Co., Ltd.) was coated on a bismaleimide/triazine resin (commonly known as BT resin) substrate, followed by UV drying, exposure, and curing (150°C, 1 hour) to yield a solder resist layer (thickness = 50 µm) on the BT substrate; this was employed as an adherend. Glass plate, aluminum plate, nickel plate, and copper plate were also evaluated as adherends. About 1 cm<sup>3</sup> of the curable silicone composition was coated on each

adherend followed by heating in an oven for 2 hours at 125°C and then heating in an oven for 2 hours at 180°C to give the adhesion evaluation test specimen. The cured product was subsequently peeled from the test specimen using a dental spatula and the adhesiveness was visually inspected under a microscope and scored on the following scale:

5 + = cohesive failure,

Δ = peeling at the interface with a thin layer remaining, and

✗ = peeling at the interface.

Thermal conductivity of the cured product

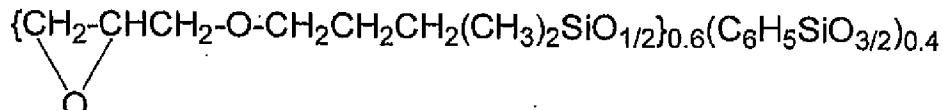
[0044] The thermal conductivity was determined from the relationship between 10 thickness and thermal resistance using a thermal resistance measurement instrument from Hitachi. The test specimen was fabricated by heating the curable silicone composition for 2 hours in an oven at 125°C and then for 2 hours in an oven at 180°C.

Flame retardancy

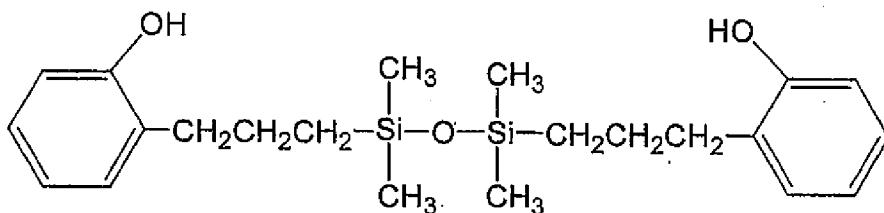
[0045] A strip-shaped test specimen (thickness 5 mm × width 10 mm × length 50 mm) 15 was fabricated by heating the curable silicone composition in an oven for 2 hours at 125°C and then for 2 hours in an oven at 180°C. The burning time of the test specimen was measured based on the UL94V-0 vertical burning test set out by Underwriters Laboratories Inc.

[Practical Example 1]

20 [0046] The following were mixed to give a curable silicone composition: 3.5 parts by mass of an organopolysiloxane (mass-average molecular weight = 1,000, viscosity = 1,290 mPa·s, epoxy equivalent weight = 276) with the following average unit formula:



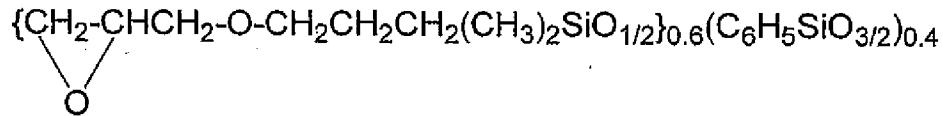
25 5.5 parts by mass of an organopolysiloxane (viscosity = 3,050 mPa·s) with the following formula:



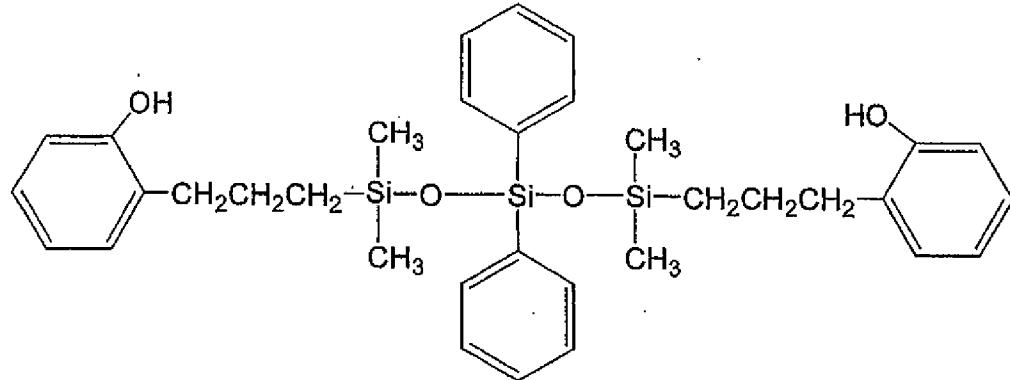
(this amount gave a molar ratio of phenolic hydroxyl in this component to the total epoxy in this composition of 1.0), 1.0 part by mass of an encapsulated amine-type cure accelerator comprising bisphenol A-type epoxy resin containing 40 mass% of amine-type cure accelerator (HX-3088 from Asahi Kasei Corporation), and 90 parts by mass of silver flake (product of Fukuda Metal Foil & Powder Co., Ltd., 50% average particle size = 5 to 15  $\mu\text{m}$ , apparent density = 2.5 to 4.0 g/cm<sup>3</sup>). The content of silver flake in this composition was 47.4 volume%. This composition was vacuum defoamed and then evaluated for its viscosity, complex viscoelastic modulus, adhesiveness, and flame retardancy by the methods described above. The results are reported in Table 1.

10 [Practical Example 2]

[0047] The following were mixed to give a curable silicone composition: 3.5 parts by mass of an organopolysiloxane (mass-average molecular weight = 1,000, viscosity = 1,290 mPa·s, epoxy equivalent weight = 267) with the following average unit formula:



15 5.5 parts by mass of an organopolysiloxane (viscosity = 3,800 mPa·s) with the following formula:



(this amount gave a molar ratio of phenolic hydroxyl in this component to the total epoxy in this composition of 1.0): 1.0 part by mass of an encapsulated amine-type cure accelerator comprising bisphenol A-type epoxy resin containing 40 mass% of amine-type cure accelerator (HX-3088 from Asahi Kasei Corporation), and 90 parts by mass of silver flake (product of Fukuda Metal Foil & Powder Co., Ltd., 50% average particle size = 2 to 15  $\mu\text{m}$ , apparent density = 2.0 to 3.5 g/cm<sup>3</sup>). The content of silver flake in this composition

was 47.4 volume%. This composition was vacuum defoamed and then evaluated for its viscosity, complex viscoelastic modulus, adhesiveness, and flame retardancy by the methods described above. The results are reported in Table 1.

[Comparative Example 1]

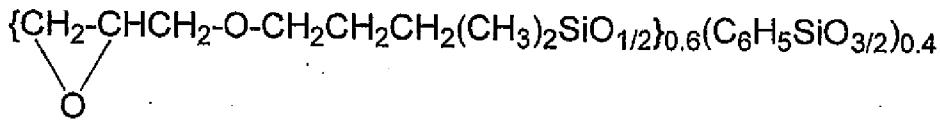
5 [0048] The following were mixed to give a curable epoxy composition: 5.0 parts by mass of a bisphenol A-type liquid epoxy resin (Epikote 828 from Japan Epoxy Resin Co., Ltd., viscosity = 15 mPa·s, epoxy equivalent weight = 190), 4.0 parts by mass of a liquid phenol compound (MEH8000H from Meiwa Plastic Industries, Ltd., this amount gave a molar ratio of phenolic hydroxyl in this component to the total epoxy in this composition of 1.0), 1.0 part by mass of an encapsulated amine-type cure accelerator comprising bisphenol A-type epoxy resin containing 40 mass% of amine-type cure accelerator (HX-3088 from Asahi Kasei Corporation), and 90 parts by mass of silver flake (product of Fukuda Metal Foil & Powder Co., Ltd., 50% average particle size = 5 to 15  $\mu\text{m}$ , apparent density = 2.5 to 4.0 g/cm<sup>3</sup>). The content of silver flake in this composition was 47.4

10 volume%. This composition was vacuum defoamed and then evaluated for its viscosity, complex viscoelastic modulus, adhesiveness, and flame retardancy by the methods described above. The results are reported in Table 1.

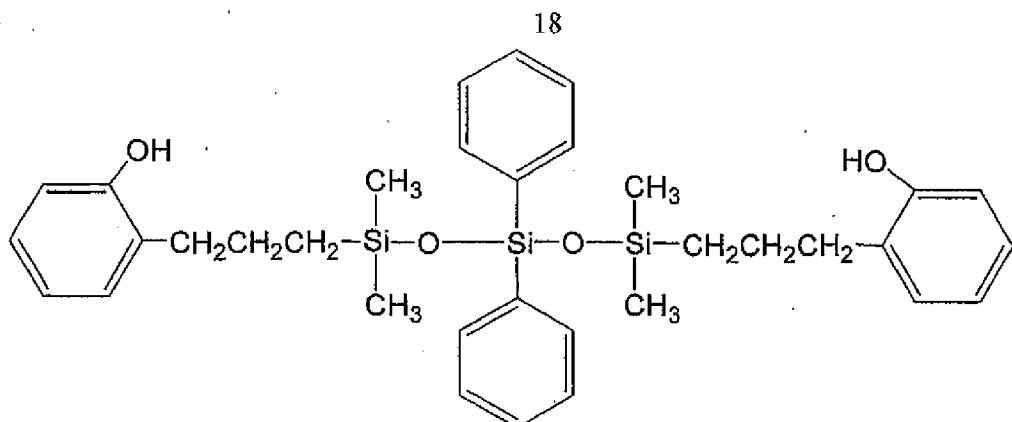
15

[Comparative Example 2]

20 [0049] The following were mixed to give a curable silicone composition: 17.0 parts by mass of an organopolysiloxane (mass-average molecular weight = 1,000, viscosity = 1,290 mPa·s, epoxy equivalent weight = 267) with the following average unit formula:



21.0 parts by mass of an organopolysiloxane (viscosity = 3,800 mPa·s) with the following formula:



(this amount gave a molar ratio of phenolic hydroxyl in this component to the total epoxy in this composition of 1.0): 1 part by mass of 3-glycidoxypropyltrimethoxysilane, 1.0 part by mass of an encapsulated amine-type cure accelerator comprising bisphenol A-type

5 epoxy resin containing 40 mass% of amine-type cure accelerator (HX-3088 from Asahi Kasei Corporation), and 60 parts by mass of spherical fused silica powder (Admafine from Admatechs Co., Ltd., 50% average particle size = 1.3 to 2.0  $\mu\text{m}$ ). The content of silica powder in this composition was 57.1 volume%. This composition was vacuum defoamed and then evaluated for its viscosity, complex viscoelastic modulus, adhesiveness, and

10 flame retardancy by the methods described above. The results are reported in Table 1.

[Comparative Example 3]

**[0050]** The following were mixed to give a curable silicone composition: 0.9 parts by mass of a dimethylvinylsiloxy-endblocked dimethylpolysiloxane with a viscosity of 20 mPa·s, 6.2 parts by mass of a dimethylvinylsiloxy-endblocked dimethylpolysiloxane with a

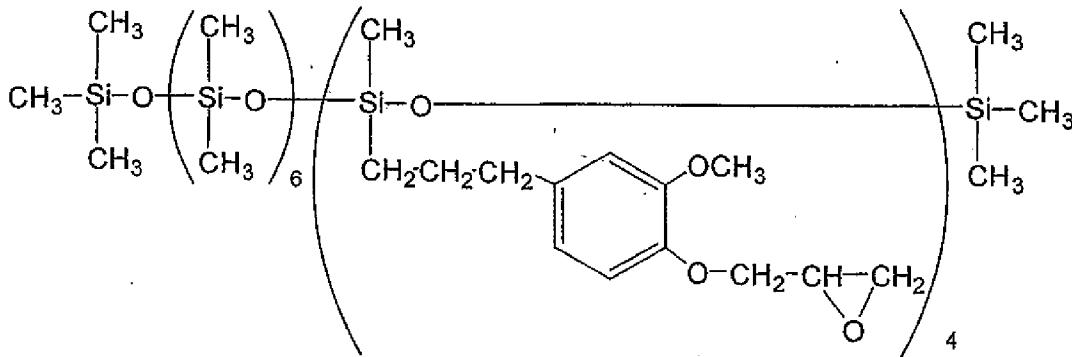
15 viscosity of 4 mPa·s, 0.8 parts by mass of trimethylsiloxy-endblocked methylhydrogensiloxane-dimethylsiloxane copolymer (silicon-bonded hydrogen atom content = 0.75 mass%), 90.5 parts by mass of silver flake (product of Fukuda Metal Foil & Powder Co., Ltd., 50% average particle size = 5 to 15  $\mu\text{m}$ , apparent density = 2.5 to 4.0 g/cm<sup>3</sup>), isopropanolic chloroplatinic acid solution (in an amount giving a platinum

20 concentration in this composition of 10 ppm), and 1.0 part by mass of 3-glycidoxypropyltrimethoxysilane. The content of silver flake in this composition was 47.4 volume%. The thermal expansivity and complex viscoelastic modulus were evaluated by the methods described above, with the exception that after vacuum defoaming the composition was cast into a mold and heated for 1 hour in an oven at 150°C. The

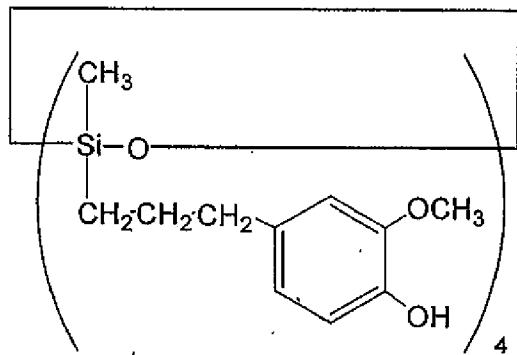
adhesiveness and flame retardancy were evaluated by the methods described above. The results are reported in Table 1.

[Comparative Example 4]

[0051] The following were mixed to give a curable silicone composition: 20.0 parts by 5 mass of an organopolysiloxane (mass-average molecular weight = 1,008, viscosity = 1,180 mPa·s, epoxy equivalent weight = 371) with the following formula:



18.0 parts by mass of an organopolysiloxane (viscosity = 840 mPa·s) with the following formula:



10

(this amount gave a molar ratio of phenolic hydroxyl in this component to the total epoxy in this composition of 1.0): 1.0 part by mass of an encapsulated amine-type cure accelerator comprising bisphenol A-type epoxy resin containing 40 mass% of amine-type cure accelerator (HX-3088 from Asahi Kasei Corporation), and 60.0 parts by mass of 15 spherical noncrystalline silica (Admafine from Admatechs Co., Ltd., 50% average particle size = 1.5 µm). The content of silica powder in this composition was 57.1 volume%. This composition was vacuum defoamed and then evaluated for its viscosity, complex viscoelastic modulus, adhesiveness, and flame retardancy by the methods described above. The results are reported in Table 1.

[0052]

Table 1

Example No.	Practical Examples		Comparative Examples			
	Pr. Ex. 1	Pr. Ex. 2	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Properties						
Viscosity (Pa·s)	450	500	> 1,000	200	30	30
Complex modulus (MPa)	500	500	3,000	100	10	60
Adhesiveness						
Solder resist	+	+	+	+	×	+
Nickel	+	+	+	+	×	+
Copper	+	+	+	+	×	+
Aluminum	+	+	+	+	+	+
Glass	+	+	+	+	+	+
Burning time (sec.)	2	3	entirely burned	entirely burned	entirely burned	entirely burned
Thermal conductivity (°C/W)	4.0	4.0	4.0	< 0.5	2.5	< 0.5

Industrial Applicability

5 [0053] The curable silicone composition of the present invention, because it exhibits good handling characteristics, can be used by such methods as transfer molding, injection molding, potting, casting, powder coating, immersion coating, dripping, and so forth. In addition, because the composition cures rapidly, a shorter heating time or a lower thermosetting temperature can be used in its molding process and the internal stresses 10 caused by thermal expansion in the molding process can thereby be reduced. This can prevent component damage when the composition is used as a protective material for small, fragile components and can provide tight adhesion with substrate. Moreover, the composition, because it exhibits good adhesion to difficult-to-adhere substrates such as solder resists, nickel, and copper, is useful, for example, as a sealant, casting agent, coating

agent, and adhesive for electrical/electronic components. In particular, cured product provided by the cure of the composition, because it has an excellent thermal conductivity, flexibility, and flame retardancy, is very useful as an adhesive between semiconductor devices and heat sinks.

CLAIMS

1. A curable silicone composition comprising:
  - (A) an organopolysiloxane that is represented by the average unit formula:
$$(R^1_3SiO_{1/2})_a(R^2_2SiO_{2/2})_b(R^3SiO_{3/2})_c(SiO_{4/2})_d$$
(wherein  $R^1$ ,  $R^2$ , and  $R^3$  are each independently selected from substituted or unsubstituted monovalent hydrocarbon groups and epoxy-functional monovalent organic groups, with the proviso that at least 20 mole% of  $R^3$  are aryl groups, and  $a$ ,  $b$ ,  $c$ , and  $d$  are numbers that satisfy  $0 \leq a \leq 0.8$ ,  $0 \leq b \leq 0.8$ ,  $0.2 \leq c \leq 0.9$ ,  $0 \leq d \leq 0.8$ , and  $a + b + c + d = 1$ ),  
5 and that has at least two of the aforementioned epoxy-functional monovalent organic groups in each molecule;
  - (B) a compound that has a group capable of reacting with the epoxy group;
  - (C) a cure accelerator; and
  - (D) a thermally conductive filler.
- 15 2. The curable silicone composition according to Claim 1, wherein the epoxy-functional monovalent organic group in component (A) is a glycidoxylalkyl group, epoxycycloalkylalkyl group, or oxiranylalkyl group.
3. The curable silicone composition according to Claim 1, wherein the group in component (B) that is capable of reacting with the epoxy group is a phenolic hydroxyl group.  
20
4. The curable silicone composition according to Claim 3, wherein component (B) is an organosiloxane that contains at least two phenolic hydroxyl groups in each molecule.
5. The curable silicone composition according to Claim 4, wherein component (B) is an organosiloxane represented by the general formula:  
25
$$R^4_3SiO(R^4_2SiO)_mSiR^4_3$$
(wherein each  $R^4$  is independently selected from substituted or unsubstituted monovalent hydrocarbon groups and phenolic hydroxyl-functional monovalent organic groups, with the proviso that at least two of the groups  $R^4$  in the molecule are said phenolic hydroxyl-functional monovalent organic groups, and  $m$  is an integer from 0 to 1,000).

6. The curable silicone composition according to Claim 1, wherein the content of component (B) is 0.1 to 500 parts by mass per 100 parts by mass of component (A).
7. The curable silicone composition according to Claim 1, wherein component (C) is an encapsulated amine-type cure accelerator.
- 5 8. The curable silicone composition according to Claim 1, wherein the content of component (C) is 0.01 to 50 parts by mass per 100 parts by mass of component (A).
9. The curable silicone composition according to Claim 1, wherein component (D) is silver powder.
10. The curable silicone composition according to Claim 1, wherein the content of component (D) is 100 to 5,000 parts by mass per 100 parts by mass of the total of components (A) and (B).
11. The curable silicone composition according to Claim 1, that additionally contains a filler (E) other than component (D).
12. A cured product obtained by the cure of a curable silicone composition according to any of Claims 1 to 11.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/JP2006/309218

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C08L83/06 C08G59/30 C09D183/06 H01L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C08L C08G H01L C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 2005/044920 A (DOW CORNING TORAY SILICONE CO., LTD; MORITA, YOSHITSUGU; ISSHIKI, MINO) 19 May 2005 (2005-05-19) the whole document	1-12
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 09, 31 October 1995 (1995-10-31) & JP 07 161740 A (SUMITOMO BAKELITE CO LTD), 23 June 1995 (1995-06-23) abstract	1-12
A	US 2003/212230 A1 (RUBINSZTAJN MALGORZATA IWONA ET AL) 13 November 2003 (2003-11-13) paragraph [0015] – paragraph [0023] paragraph [0035] – paragraph [0037]	1-12

Further documents are listed in the continuation of Box C.

See patent family annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the International filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the International filing date but later than the priority date claimed

- \*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the International search

14 July 2006

Date of mailing of the International search report

28/08/2006

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Contet, F

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/JP2006/309218

## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 08, 29 August 1997 (1997-08-29) & JP 09 095651 A (SUMITOMO BAKELITE CO LTD), 8 April 1997 (1997-04-08) abstract -----	1-12

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No  
PCT/JP2006/309218

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 2005044920	A 19-05-2005	NONE		
JP 07161740	A 23-06-1995	JP 2834658 B2		09-12-1998
US 2003212230	A1 13-11-2003	US 2003071366 A1		17-04-2003
JP 09095651	A 08-04-1997	JP 3313267 B2		12-08-2002